

## EFFECTS OF MICROGRAVITY ON THE FORMATION OF AEROGELS

A. J. Hunt, M. R. Ayers,  
Lawrence Berkeley National Lab.,  
University of California,  
Berkeley, CA 94720  
510-486-5370; ajhunt@lbl.gov

R. J. Cronise, D. A. Noever  
NASA/Marshall Space Flight Center  
Huntsville, AL 35812  
256-544-5493  
Raymond.Chronise@.msfc.nasa.gov

555-29  
037132

L. Sibille  
Universities Space Research Association,  
NASA/Marshall Space Flight Center,  
Huntsville, AL 35812  
256-544-5221  
Laurent.Sibille@.msfc.nasa.gov

### Introduction

This paper describes research to investigate fundamental aspects of the effects of microgravity on the formation of the microstructure of metal oxide alcogels and aerogels. We are studying the role of gravity on pore structure and gel uniformity in collaboration with Marshall Space Flight Center (MSFC) on gelling systems under microgravity conditions. While this project was just initiated in May 1998, related research performed earlier is described along with the plans and rationale for the current microgravity investigation to provide background and describe newly developing techniques that should be useful for the current gellation studies

The role of gravity in materials processing must be investigated through the study of well-mastered systems. Sol-gel processed materials are near-perfect candidates to determine the effect of gravity on the formation and growth of random clusters from hierarchies of aggregated units. The processes of hydrolysis, condensation, aggregation and gellation in the formation of alcogels are affected by gravity and therefore provide a rich system to study under microgravity conditions. Supercritical drying of the otherwise unstable wet alcogel preserves the alcogel structure produced during sol-gel processing as aerogel. Supercritically dried aerogel provides for the study of material microstructures without interference from the effects of surface tension, evaporation, and solvent flow.

Aerogels are microstructured, low density open-pore solids. They have many unusual properties including: transparency, excellent thermal resistance, high surface area, very low refractive index, a dielectric constant approaching that of air, and extremely low sound velocity. Aerogels are synthesized using sol-gel processing followed by supercritical solvent extraction that leaves the original gel structure virtually intact.

These studies will elucidate the effects of microgravity on the homogeneity of the microstructure and porosity of aerogel. The presence of poorly controlled microporosity in aerogel leads to material non-uniformity that gives rise to increased light scattering. Investigation of the effect of gravity driven solute flows within microclusters and their effect on condensation and agglomeration reactions will enable us to improve the preparation and properties of aerogel. Increased clarity of images viewed through aerogel and decreased scattering from the pores of aerogel will significantly improve the prospects for large-scale adoption of aerogel in such applications as transparent insulating windows, high performance thermal insulation, and Cherenkov detectors.

## Experimental Method

We are investigating alternative methods to initiate gellation in alkoxide sols. In conventional sol-gel processing, catalysts are introduced in the water-containing phase prior to initiating the reactions by mixing with the alkoxide. Our new approach involves ultraviolet radiation to control the catalysis. This approach was developed for two principle reasons. First, to study the effect of controlling catalysis and associated solvent releases and heat generation in microgravity conditions. Ultraviolet initiated catalysis offers a unique ability to effect the rate of gellation and condensation reactions on demand. Secondly, the approach is better suited to space based experimental conditions. Rapid mixing of the alkoxide-solvent and water-solvent-catalysis solutions is usually achieved by modified syringe pump setups that break a membrane between two opposing volumes and rapidly mix the two components. This process is often associated with bubble formation that can persist in microgravity conditions. These bubbles interfere with several sample analysis techniques used to determine material properties.

Short-wave UV is capable of cleaving many of the bonds found in alkoxide-based silica sols, such as, O-H, O-R, C-C, and C-H. However, the only effects of UV on SiO<sub>2</sub> gels has been reported for thin-films [1, 2]. In these cases, UV exposure significantly increased the rate of gellation and the densification of the final xerogel. However, the effects of UV on the microstructure and porosity of large silica monoliths was not reported until this work.

The effects of pH on gel microstructure, porosity, and clarity have been reported earlier [3-6]. These show a strong dependence on pH in both primary particle growth and aggregation of particles and clusters into a gel. Additionally, even small amounts of acid or base catalysts greatly increase the rate of gellation in alkoxide-derived silica sols. As we desired to study sols with long gel times, we studied the effects of UV on sols with no added catalyst, and report the microstructural characteristics of the resulting gels and aerogels, determined by light scattering, surface area measurements, TEM and x-ray diffraction.

Gel preparation utilized precondensed TEOS ("Silbond H-5", Silbond Corp.), anhydrous ethanol (UV grade), and high purity water. The sol was prepared by mixing two solutions prepared from the starting compounds. The mixed sol was divided into 4 equal portions and poured into fused-silica tubes and sealed by PTFE plugs with viton o-rings. Samples were exposed to ultraviolet light from two 15 Watt germicidal Hg-vapor lamps, in an enclosed light-box. Samples were exposed for various lengths of time (T<sub>UV</sub>), including, no exposure, 5 hours, T<sub>UV</sub> = gel time and continuous exposure. After exposure, the samples were kept in the dark. The temperature of the samples in the light box were kept constant at about 25 °C).

The evolution of light scattering with time was measured at 532 nm with a doubled Nd-YAG c.w. laser at a 90° scattering angle. Samples were removed from UV exposure at regular intervals and their scattering measured and calibrated against a sealed CS<sub>2</sub> standard. When the scattering intensity stabilized with respect to time for all samples, the gels were removed from their holders and soaked in 30% H<sub>2</sub>O/ethanol for 48 hours. Water was removed from the gels by four successive soaks in 200 proof ethanol for 24 hours each. The aged alcogels were dried using standard CO<sub>2</sub>-substitution and supercritical drying in a 300 ml Polaron critical-point dryer. Single-point B.E.T. surface area measurements of the dried aerogels were obtained from the desorption isotherm of 30% N<sub>2</sub>/He using a Quantasorb analyzer. UV-visible transmission spectra, X-ray diffraction powder patterns,

and high resolution TEM images were taken. Samples for TEM analyses were ground in acetone, and evaporated onto holey carbon-Cu grids.

## Results and Discussion

Table 1 lists several physical of the characteristics of UV-catalyzed neutral silica sols, gels, and aerogels. First, a significant decrease in the gel time (to about one third) is observed with continuing UV irradiation times. This is consistent with a general increase in the rate of hydrolysis and condensation reactions leading to gellation.

Table 1. Characteristics of UV catalyzed sol, gel, and aerogels.

Sample	TUV	TGEL	~Slope	%T = $A \exp(-Bt/l^4)$		Surface area m <sup>2</sup> /gm
	hours	hours	(scat. vs. time)	(A)	(B)	
1	0	720	6	0.5762	0.3260	480
2	5 ( $\ll$ TGEL)	720	6	0.5570	0.3370	550
3	250 (= TGEL)	250	6, then 2	0.5724	0.3651	520
4	1900 ( $\gg$ TGEL)	250	6	0.5504	0.3790	400

Light scattering is an effective monitor of the evolving structure of gel systems [7]. The technique is most sensitive during the formation of clusters and their aggregation into a network gel [8]. The growth characteristics of these clusters can be observed by plotting the log of the scattering intensity vs. the log of time. Spherical or compact cluster growth has a characteristic a slope of six (acid catalyzed) and linear growth in higher surface charge conditions produces a slope of two (base catalyzed) [7]. This occurs because volume evolves as the cube of time for spherical growth (and polarizability to the sixth power), while linear growth produces a first power volume (and second power polarizability) increase with time. In this study, the neutral silica sols all show a slope of six, consistent with the formation of weakly acidic Si-OH groups formed by the initial hydrolysis of Si-OR groups. A dramatic exception to this is seen when UV light exposure is ceased at TGEL wherein the slope changes to two when UV is discontinued. As the aggregation of clusters during gellation is controlled by the surface potential of the clusters, it is likely that recombination products of photo-degraded species increase the surface charge on growing clusters. This in turn affects the formation behavior by shifting the manor of assembly from cluster like to chain like aggregation.

Light scattering from internal features such as the large pore fraction is the primary cause of the wavelength-dependent Rayleigh scattering and result in the bluish cast of dried silica aerogels[9]. Larger features, in the aerogel such as surface damage due to solvent flows, scratches, and larger occlusions such as bubbles, can also contribute to scattering. These two effects can be separated and quantified using the equation [7]:

$$T = A \exp(-Bt / \lambda^4)$$

where T is the % transmittance of an aerogel of thickness,  $t$ , at a wavelength,  $\lambda$ , and A and B are constants. Fitting the UV-visible spectrum of an aerogel to this equation gives A (the wavelength independent portion of scattering, due to large features) and B (the wavelength dependent portion, due to the internal gel structure). Values of A and B appear in Table 1. All samples show an increase in B with longer UV exposure, indicating a coarsening of the gel structure due to UV light. A general decrease in surface area of the dried aerogels is also seen with prolonged UV exposure of the alcogel. Both of these effects indicate an enhancement of dissolution and re precipitation reactions leading to both pore and particle growth.

TEM images for dried aerogels where  $T_{UV} = T_{GEL}$ , and  $T_{UV} \gg T_{GEL}$  show rather large primary particles (compared to base-catalyzed aerogels) in accord with the lower surface area of these aerogels. The image of the  $T_{UV} = T_{GEL}$  sample shows a rather open structure as anticipated for a gel with a certain amount of linear cluster aggregation. The sample with  $T_{UV} \gg T_{GEL}$  shows a more dense compacted structure, consistent with spherical cluster growth. Both samples appeared predominantly amorphous to the electron beam. However, *some areas* of the sample  $T_{UV} = T_{GEL}$  showed higher levels of crystallinity.

The X-ray powder patterns showed typical amorphous pattern for samples with  $T_{UV} = 0$ ,  $T_{UV} \gg T_{GEL}$ . However, the  $T_{UV} = T_{GEL}$  sample shows a significantly different pattern, that is very broad (as expected for <10 nm particles), but similar to that found for dehydrated  $H_2Si_4O_8$  precipitates [10]. Long-term aging of sol-gel sodium aluminosilicate gels has been shown to form increased numbers of crystallization nuclei compared to gels dried soon after gellation [11]. However, in our study, crystallinity is only observed when UV exposure was ceased at the gel point, and then only in a portion of the aerogel. It is likely that UV exposure forms dense  $SiO_2$  particles by enhancement of internal condensation reaction of surface -OH groups. These particles can then act as crystallization centers as particle growth continues very slowly after ceasing UV exposure.

## Future Plans

Increased comprehension of gel formation processes will benefit the broad understanding of sol-gel chemistry. In particular, the clarification of the effect of solvent flows on cluster growth and gel aggregation processes measured under microgravity conditions in KC 135 and shuttle flights will help settle controversy over which of the various models of gel formation is correct. Time resolved light scattering measurements will be used in studies of sol growth and gel formation. Additional measurements on supercritically dried aerogels including angle and polarization dependent Mueller scattering matrix determination, High Resolution Transmission Microscopy, x-ray, and BET pore size analysis will provide detailed information as to the uniformity and size of the micropore structure. Thus, research into microgravity effects will advance both practical applications for aerogel as well as fundamental sol-gel science. Aerogel is being developed for a range of applications in the commercial and aerospace arenas. Thus improvements in processing gained through microgravity research can be used to produce better aerogel products.

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